

UNIVERSITY OF PENNSYLVANIA

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LUMINOSITY OF RADIUM
COMPOUNDS

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A THESIS

IN PHYSICS

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN PARTIAL
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Reprint from
The Physical Review, Vol. XXIII, No. 4

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ABSTRACT

Effect of temperature on the luminosity of RaBr_2 and of mixtures with BaBr_2 .

—(1) In the case of pure RaBr_2 , a tube containing 9 mg after heating to 600°C gave an initial luminosity of $5600^\circ \mu\text{-candles/cm}^2$ which decreased in 1 hr to 3600 or 2800 according as the tube was cooled to 20° suddenly or gradually, and continued to decrease, according to the equation $I_t = I_\infty + I_0 e^{-At/67}$, reaching an equilibrium value of only $6\mu\text{-c/cm}^2$ after 500 hours. This equilibrium value increases somewhat with the temperature but depends only on the temperature and not on the previous treatment. (2) In the case of mixtures with BaBr_2 , the initial luminosity after removing from the furnace increases exponentially with the temperature; the rate of decay is greater the lower the temperature at which the sample is held; the equilibrium luminosity for 1 to 3 per cent RaBr_2 at 20° increases markedly as the radium content decreases and for higher temperatures decreases as the temperature is increased. For 7 per cent RaBr_2 , however, the equilibrium luminosity at 20° is less than for either 3 or 100 per cent, and it increases with the temperature. In all cases, however, the equilibrium value depends only on the composition and on the temperature at which it is kept. These results are consistent with the suggestions by Rutherford of the formation of "active centers."

I. INTRODUCTION

SYSTEMATIC investigation of luminous compounds was undertaken first in 1910 by Marsden¹ who found that alpha particles from an emanation tube bombarding zinc sulfide imparted to it a luminosity that decreased more rapidly than the emanation causing it. Rutherford² explained this phenomenon by the presence in the zinc sulphide of active centers whose destruction was accompanied by the emission of light. According to this theory, (1) the brightness of the compound was dependent on the rate of destruction of these active centers, (2) the brightness decay followed an exponential law, and (3) the brightness should ultimately reach a zero value.

Patterson, Higgins and Walsh,³ experimenting in the National Physics Laboratory in London, found that the luminosity decay curves of zinc sulfide, although exponential for the first part of the life of the compounds, approached a constant value, and that the luminosity never would become zero. To explain this, Walsh assumed that while active centers were being destroyed, others were being formed, and that equilibrium

¹ Marsden, *Proc. Roy. Soc.*, A **83**, 548-561, (1909-10)

² Rutherford, *Proc. Roy. Soc.*, A **83**, 561-572, (1909-10)

³ Patterson, Higgins and Walsh, *Proc. Phys. Soc. Lon.*, **19**, 215-249, (1916-17)

luminosity occurred when the destruction rate equalled the formation rate. No effort was made to determine upon what factors the formation rate depended.

Kabakjian began in 1918 work on a new group of luminous compounds, radium bromide and barium bromide, and found that they possessed the extraordinary property of complete rejuvenation of luminosity on the application of heat. With Karrer,⁴ he undertook a systematic investigation of these compounds, which was interrupted by war conditions. The object of the present investigation is to continue this work, to investigate the luminosity decay curves of pure radium bromide and of mixtures of radium bromide and barium bromide, and to show that each compound has a definite equilibrium luminosity which is a function of the temperature at which the compound is kept.

II. METHOD OF MEASUREMENT

Five tubes were used, especially prepared by Kabakjian in such a manner as to show extremely high luminosity. The contents of the tubes are indicated in Table I.

TABLE I
Contents of tubes under investigation

Tube	RaBr ₂ (x)	BaBr ₂ (y)	100x/(x+y)
1	9.0 mg	0 mg	100
2	0.735	19.265	3.7
3	1.41	18.59	7.1
4	1.27	76.76	1.6
5	1.01	62.41	1.6

The compounds were fused in pyrex glass tubes and the tubes sealed under reduced pressure. Tubes of high radium content were used since it was found that the rate of luminosity decay was proportional to the radium content, hence the higher the content the shorter the period necessary for the investigation of any one factor.

For heating the tubes, an electric furnace, cylindrical in shape, having a heating chamber with a uniform temperature zone about 10 cm long and 2 cm in diameter was used. The temperature was measured by a quartz-enclosed platinum-rhodium thermometer and a Thwing pyrometer. A brass cylinder with cylindrical holes large enough to admit the radium tubes was used as container. This was placed in contact with the thermocouple case so that the temperature recorded by the instrument might be taken as the temperature of the radium itself. Five minutes heating in the furnace was sufficient to bring the tube to equilibrium.

⁴ Karrer and Kabakjian, Jour. Franklin Inst. (Sept. 1918)

Tube luminosities of sufficient magnitude were measured by means of a Nutting polarization photometer manufactured by Hilger and obtained from the Arthur H. Thomas Co. of Philadelphia. The optical system is indicated on the right in Fig. 1. In making an observation, the telescope is focused on the photometer cube so that the field appears as two strips of reflected light from the radium with the transmitted light from the reference lamp between them. By varying the intensity of the reference lamp by means of the Nicol prism B'' , the strip is made alternately lighter and darker than the strips illuminated by the radium until a color match is obtained.

The arrangement of apparatus is shown in Fig. 1. The reference lamp L is fed by storage batteries and maintained by a variable resistance at a definite constant voltage, indicated by the voltmeter V . The lamp is

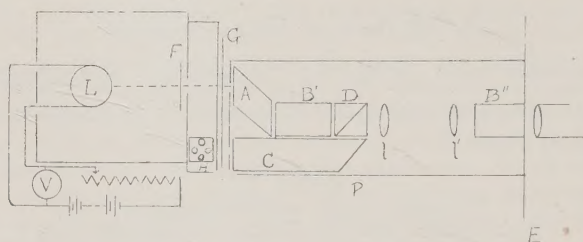


Fig. 1. Arrangement of apparatus.

- | | |
|---|----------------------------------|
| H —Carbon block containing tube under observation | |
| A, C —Reflecting prisms | B', B'' —Nicol prisms |
| D —Photometer cube | E —Disk graduated in I_s/I_r |
| l, l' —Lenses | G —Ground glass screen |

mounted on guides so that its illumination of the screen may be controlled by changing its distance from the screen as well as by changing the voltage across the lamp. Light from L falls upon the ground glass diffusing screen G after passing through the green gelatine filter F which is interposed to produce a better color match. The radium rests in a carbon block mounted on a slide immediately in front of the diffusing screen.

To determine the candle-power of the reference lamp, it was compared by means of a Lummer-Brodhun photometer with a carbon lamp standardized by the Bureau of Standards. Its candle power when operated at 80 volts was found to be 0.27; when operated at 90 volts, 0.70.

To determine the absorption of the green filter, the luminosity of a radium tube was measured with and without the green filter between the reference lamp and the photometer. The ratio of the two intensities was taken as the transmission coefficient under the conditions of use. The Purkinje effect is operative for intensities of light comparable with that of the radium, but measuring the transmission coefficient under

conditions identical with those under which the luminosity measurements were made, eliminated as far as possible errors due to this effect. Since the transmission coefficient depends on the wave-length of the light transmitted, and since the color of the light emitted by the reference lamp at 80 volts was markedly different from that emitted by the lamp when it was operated at 90 volts, the transmission coefficient of the screen was determined under both conditions.

To maintain the radium at constant temperature during photometric measurements, it was placed in a carbon block, insulated, and supplied with a convenient system of heating coils controlled by a thermometer thermostat. The slide on which the block rested was covered with a sheet of copper as was the surface of the lamp box to which the slide was attached. This increased the radiating surface and prevented charring of the wood.

The brightness of the tubes was readily calculated from the scale readings of the photometer and the constants of the apparatus. The photometer is graduated in logarithms of the ratio of the illuminating power of the reference lamp to that of the radium tube. If, then, K is the transmission coefficient of the filter, C_1 the candle-power of the reference lamp, C_2 the apparent candle-power of the radium tube, d_1 and d_2 their respective distances from the ground glass screen,

$$\log_{10} (KC_1/d_1^2) - \log_{10} (C_2/d_2^2) = \text{scale reading} = X.$$

If A is the area of the exposed luminous portion of the tube, the brightness B in apparent candle-power per square centimeter is

$$B = (KC_1 d_2^2) / (d_1^2 10^X A).$$

Measurements of tube luminosity below the scope of the instrument were made by means of a 'radium scale.' This is a series of eight tubes carefully graded in radium content so that when heated to 500° they exhibit luminosities ranging from 'just visible' to 10 microcandles per square centimeter. The brightness of the most luminous one was determined photometrically. By comparison with these the approximate luminosity of low intensity tubes could be determined. For quantitative work the scale is of little value; it is possible, however, by its use to determine with a high degree of certainty whether or not a tube has reached a definite equilibrium value.

III. EXPERIMENTAL PROCEDURE AND RESULTS

1. *Determination of time-luminosity curves.* To determine the time rate of decay of luminosity of a tube at a given temperature θ , the tube was heated to any desired temperature θ_0 , then allowed to cool to the required temperature θ and maintained at that temperature. Its lumin-

osity was read at half to one hour intervals for the first day, at longer intervals on succeeding days. Experimental results for typical time-luminosity curves of tubes 1 and 2 are given in Fig. 2.

Analysis of curves for tubes 1, 2, and 3 for temperature limits 600° – 20° C taken in this way, shows that (1) the initial luminosity of c.p. radium bromide is many times that of mixtures of radium bromide and barium bromide; (2) the initial luminosities of the mixtures are almost

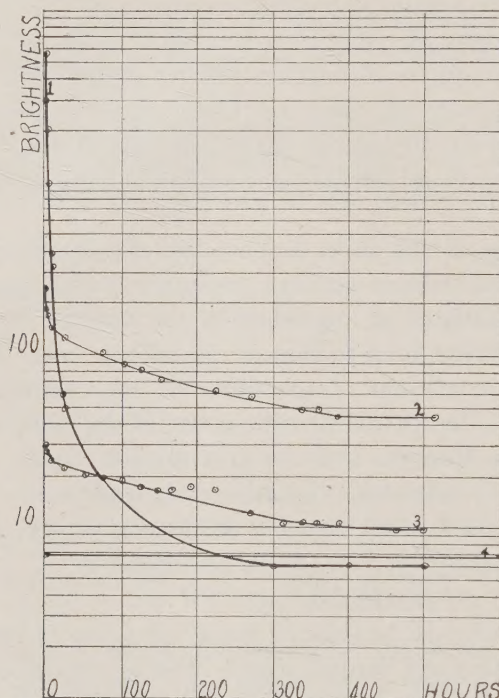


Fig. 2. Time-luminosity curves

Curve	Tube	Initial temperature	Temperature of observation
1	1	600° C	20° C
2	2	600	20
3	2	600	150
4	2	150	150

directly proportional to the per cent of radium bromide present; (3) the rate of decay was much greater for c.p. radium bromide than for the mixture, but that the luminosity decay curves were of similar form for all the tubes investigated; (4) each tube reached an equilibrium luminosity that varies in inverse order with the radium bromide content.

An empirical formula for the variation in luminosity with time was obtained from consideration of a typical time-luminosity curve for

$\log \log I_0/(I_t - I_\infty)$ plotted against $\log t$ (see Fig. 3). After the first hour, the curve is a straight line which may be represented by the equation:

$$I_t = I_\infty + I_0 e^{-At^B}$$

For example, for tube No. 1 (initial temperature 600°C ; temperature of observation 20°C) we have

$$I_t = 6 + 6960 e^{-.267t^{.67}} (\mu\text{c}/\text{cm}^2),$$

where t is in hours.

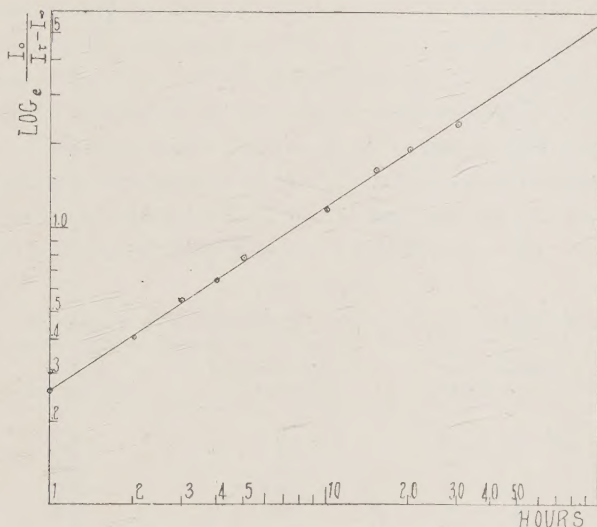


Fig. 3. Time-luminosity curve for tube 1.

I_0 —Intensity of the reference lamp

I_t —Intensity of the radium light

2. *Factors affecting initial luminosity.* Further investigation of the factors affecting initial luminosities of the tubes made it apparent that the initial luminosities were reproduced at will provided that certain conditions were exactly reproduced. The controlling conditions were found to be (1) the initial temperature of the tube; (2) the rate at which it was cooled.

(1) The effect of initial temperature on initial luminosity was studied with tube No. 2. The luminosity of this was measured at 18°C , after it had reached equilibrium value. The tube was then heated to 260°C or some higher temperature and the luminosity measured five minutes after removal from the furnace. The results appear in Curve 1 of Fig. 4, in which the initial luminosity is plotted against temperature. The drop in luminosity at 690° is due probably to escape of emanation at that temperature.

On plotting on semi-logarithmic paper initial luminosity against temperature (Curve 2, Fig. 4), a straight line is obtained. This indicates that the curve may be represented by the empirical equation

$$I_{\theta} = 1.85 e^{1.56\theta}$$

in which θ is the temperature centigrade.

(2) The effect of rate of cooling is illustrated by the observations on the c.p. RaBr_2 tube No. 1. This tube was heated to 600°C , permitted to cool at various rates, and observed one hour after removal from the

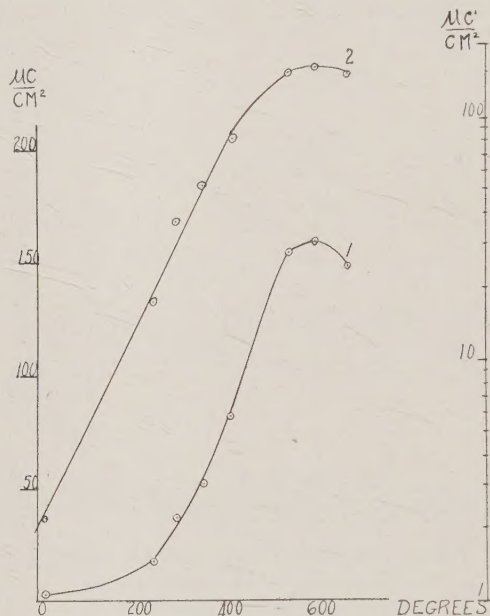


Fig. 4. Initial luminosity at various temperatures for tube 2. Curve 1 is based on the left hand scale, Curve 2 on the right hand scale. Luminosity was measured 5 min. after removal from the furnace.

furnace. The results are cited in Table II. It is seen that when cooled in 2 min. the luminosity is nearly 30 per cent greater than when cooled in 30 min. Similar results were observed in tubes 2, 3, 4 and 5, but were not measured photometrically.

TABLE II

<i>Effect of rate of cooling on luminosity of pure RaBr_2</i>	
Initial temperature 600°C ;	temperature of observation 20°C
Time of cooling	Brightness 1 hour after removal from furnace
2 min.	3610 $\mu\text{C}/\text{cm}^2$
5	3480
10	3210
20	2830
30	2800

3. *Equilibrium luminosity.* The time-luminosity curves for temperature limits 600-20° showed that each tube reached an equilibrium luminosity dependent on the compound used. Other curves for temperature limits 600-100° and 600-150° showed that the equilibrium luminosity of each tube is dependent on the temperature at which the tube is kept. In order to investigate the possible effect of previous history on equilibrium luminosity of a tube at a given temperature, tubes No. 2 and No. 3, having decayed to equilibrium luminosity at 20° C were heated to 100°C and the time-luminosity curves taken at that temperature. The equilibrium luminosity so measured agreed in each case with that obtained by the previous method for the same temperature. The equilibrium luminosities at 150° C obtained by the two methods also agree, as indicated in Table III. *The equilibrium luminosity of a tube is dependent, therefore, on the content and temperature of the tube only*, and is independent of the previous history of the tube. Table III summarizes the experiments on equilibrium luminosity for tubes No. 2 and No. 3.

TABLE III

Summary of the Experiments on Equilibrium Luminosity.

Initial temperature	Temperature of observation	Equilibrium luminosity ($\mu\text{c}/\text{cm}^2$)	
		Tube 3	Tube 2
600° C	20° C	1.0 $\mu\text{c}/\text{cm}^2$	45
600	100	2.21	12.5
600	150	6.9	6.9
100	100	2.2	12.5
150	150	6.9	6.9

The equilibrium luminosity of pure radium bromide varied much less for temperature changes within the range of temperatures used than the tubes containing a mixture of radium and barium bromides. On heating it to 100° and 150° respectively, slight increases in luminosity were observed but were of insufficient intensity for photometric measurement. Its behavior in this respect was similar to that of tube 3 containing 7 per cent radium bromide. Tube 2 of lower radium content exhibited a marked decrease in luminosity with increased temperature, a property displayed also by tubes of still lower radium content. An extended investigation of a large number of tubes of carefully graded radium content, when subjected to wide range of temperatures, is necessary to establish the luminosity-temperature-content relation. This involves measurement of much lower luminosities than the method described in this paper permits. A more flexible method is being developed that, it is hoped, will make possible the measurements required.

4. *Rate of decay.* A limited investigation of the effect of low temperatures on the rate of decay of luminosity of these compounds showed that

decreased temperature causes an increase in rate of luminosity decay. Two tubes, No. 4 and No. 5, prepared from the same mixture and therefore identical in composition, were heated to 600° C, cooled to room temperature and their luminosity measured. One tube was then placed in liquid air and the other maintained at room temperature. After nineteen hours the luminosity of the tube kept at room temperature had decayed to 83 per cent of its maximum value, and that of the tube kept at liquid air temperature to 68 per cent of its maximum value. Both tubes were reheated to 600° C and the process repeated with the tubes interchanged. Similar results were observed.

5. *Effect of subsequent heating on the luminosity of tubes.* Tubes (No. 4 and No. 5) heated to 600°, cooled suddenly to 20°, and subsequently heated successively to eight temperatures ranging from 40° to 218°, decreased in brightness as their temperature was raised. While being measured, the luminosities of the tubes would decay somewhat, but any errors caused by such normal decay during the five hours required for these measurements would not exceed 3 per cent of the maximum luminosity. The decrease in luminosity was only temporary as the tubes regained their brightness on being cooled to room temperature. Table IV gives the experimental results for tube No. 4. Those for tube No. 5 were similar.

TABLE IV
Effect of subsequent heating on luminosity of tube No. 4

Temperature of observation	Brightness
25° C	150 $\mu\text{c}/\text{cm}^2$
50	110
75	78
100	51.5
125	31.5
150	18.0
175	10
200	5

IV. DISCUSSION

As a result of this investigation certain facts are established that suggest the following explanation of the phenomenon.

It is evident that heating radium bromide to a sufficiently high temperature and cooling it, imparts to it the property of becoming luminous under bombardment of the alpha particles which it emits. Barium bromide heated and exposed to alpha particle bombardment also becomes luminous. For a given quantity of radium bromide the initial luminosity obtained from c.p. radium bromide is very much greater than that obtained from mixtures of the two bromides, but mixtures of the salts possess a relatively high equilibrium luminosity at the temperatures of observation.

If we assume that the luminosity in both cases is due to so-called active centers or unstable configurations, as Rutherford suggested in the case of zinc sulfide, it is evident that these active centers are formed on the absorption of heat energy by the compound. High temperatures followed by rapid cooling are necessary for the formation of any considerable number of them. Thermal agitation at high temperatures makes possible the instantaneous existence of large numbers of unstable configurations. Rapid decrease in agitation, incident to rapid cooling makes the instantaneous configuration permanent, other conditions remaining constant, in much the same way that rapid cooling produces crystalline steel, but gradual cooling permits the formation of a more stable form. The disintegration rate at any instant is proportional to the number of active centers present. If the luminosity of a tube depends on the rate of disintegration, it follows that rapid cooling, increasing the number of active centers present, would increase the luminosity of the tube as found in the experiments.

Maximum luminosity occurring when the tube was heated to 600°C and cooled suddenly to 20°C indicates that maximum number of active centers was formed. On subsequent heating the luminosity decreased due to the fact that increased thermal agitation decreased the susceptibility of the active centers to disintegration by alpha particle bombardment. It is probable that the active centers were not destroyed since no light was evolved as the temperature was raised.

That any one tube at a given temperature attains an equilibrium luminosity characteristic of that temperature, and never reaches zero luminosity, seems to indicate that active centers are produced at all temperatures, in numbers varying with the temperature. When the number of such centers produced at a given temperature is equal to the number destroyed, the luminosity becomes constant. According to this view, if the tubes were kept at absolute zero, the luminosities would disappear in time. This is in keeping with the fact that maintaining the compound at the temperature of liquid air considerably accelerated the decay in luminosity, due probably to the fact that very few active centers can be produced at that temperature.

In conclusion the writer wishes to express her most sincere appreciation to Dr. D. H. Kabakjian at whose suggestion and under whose direction the work was carried out, and to Dr. Horace C. Richards for his interest and many helpful suggestions.

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May 29, 1923.

